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14. ABSTRACT

This final technical report begins with the objective, followed by detailed reports on new accomplishments and new findings obtained in the project. They are presented in six sections: A. Potential Energy Surfaces of Ion-Molecule Reactions, B. Potential Energy Surfaces of Ions, C. Potential Energy Surfaces for Photochemical Reactions and Nonadiabatic Processes, D. Potential Energy Surfaces of Open-Shell Molecules, E. Dynamics and Kinetics in the Ground Electronic State and F. Potential Energy Surfaces for the Dynamics of Chemical Laser Systems. . The Publication List and Interactions/Transactions conclude the report.

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801 N. Randolph Street, Room 732, Arlington, VA 22203
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Phone: (202) 767-4963

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The Principal Investigator:
Keiji Morokuma
Department of Chemistry, Emory University,
1515 Pierce Dr., Atlanta, GA 30322
Phone: (404)-727-2180
E-mail: morokuma@emory.edu

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Abstract: This final technical report begins with the objective, followed by detailed reports on new accomplishments and new findings obtained in the project. They are presented in six sections: A. Potential Energy Surfaces of Ion-Molecule Reactions, B. Potential Energy Surfaces of Ions, C. Potential Energy Surfaces for Photochemical Reactions and Nonadiabatic Processes, D. Potential Energy Surfaces of Open-Shell Molecules, E. Dynamics and Kinetics in the Ground Electronic State and F. Potential Energy Surfaces for the Dynamics of Chemical Laser Systems. . The Publication List and Interactions/Transactions conclude the report.

1. Objectives.

Understanding the mechanism, kinetics and dynamics of elementary gas phase reactions is one of the major goals of chemistry. Such understanding is also essential to predicting and understanding plasma dynamics and optical radiation associated with the spacecraft-atmosphere interactions. The objective of the present research under the AFOSR grant (F49620-98-1-0063) is to provide, based on mainly the ab initio molecular orbital and some dynamics calculations, theoretical information concerning the potential energy surfaces (PESs) that dictate the kinetics and dynamics of gas phase elementary reactions. The major theoretical thrust of the present approach is to study more than one potential energy surfaces at the same time, paying special attention to the seam of crossing of potential surfaces (conical intersection between the states of the same spin, or crossing between the states of different spin) and to the non-adiabatic transition between them. Many of the systems for which we perform theoretical calculations are relevant to upper and lower atmospheric chemistry and chemical lasers, problems of major interest of the Air Force. They are chosen based on the excellent experimental studies by groups at Air Force Research Laboratory, in order to provide them with some new insight that is not easily available without theoretical studies.

2. Accomplishments and New Findings.

A. Potential Energy Surfaces of Ion-Molecule Reactions

A-1. Mechanism of the $C_2H_2^+$ + NH_3 reaction.

Q. Cui and K. Morokuma, Ab initio study on the mechanism of $C_2H_2^+$ + NH_3 reaction. Efficient charge transfer and proton transfer processes competing with stable complex formation. J. Chem. Phys., **108**, 4021-4030 (1998).

High level ab initio calculations have been performed to investigate the mechanism of the ion-molecule reaction $NH_3+C_2H_2^+$. Three channels, covalent complex formation (CC), proton transfer (PT) and charge transfer (CT) have been studied. Among the two pathways found for the PT channel, one leads the reactants $NH_3+C_2H_2^+$ to $NH_4^++C_2H(^2\Pi)$ through a moderately bound complex without any barrier, and the other leads $NH_3^++C_2H_2$ to the H-atom transferred products $NH_4^++C_2H(^2\Sigma^+)$ with a

modest barrier. These findings support the fast "stripping" mechanism proposed by Anderson et al. As to the CC channel, several isomers of $C_2H_5N^+$ and the isomerization transition states have been located. No significant barrier relative to the reactants have been found on either the ground or the ^2A" excited state. To rationalize the experimental fact that no CC channel products have been observed, it is argued that the reactants $NH_3+C_2H_2^+$ correlate adiabatically to excited states of covalent $C_2H_5N^+$ species, whose formation requires significant alternation of the $C_2H_2^+$ geometry and electronic structure. Therefore, the system is most likely to follow the PT or the CT channel instead of visiting the CC channel. For the CT channel, limited potential energy surface scans of the three electronic states (1,2 ^2A' + ^2A") indicate that CT at different approach angles or between electronic states of different symmetries (A'→A', A"→A') may produce final products of different characteristics, and might account for the two pathways proposed by Anderson et al.

A-2. Mechanism of the $C_2H_2^+$ + CH_4 reaction.

Q. Cui, Z. Liu and K. Morokuma, Theoretical study on the mechanism of CH_4 + $C_2H_2^+$ reaction. Mode-enhancement effect, J. Chem. Phys., **109**, 56-62 (1998).

High level ab initio calculations have been performed to investigate the mechanism of the ion-molecule reaction of CH_4 + $C_2H_2^+$. Except for some subtle differences, the profile for the H-abstraction channel obtained here at the G2M//B3PW91/6-311G(d,p) level is very similar to that found in a previous study at the G2//MP2/6-31G(d) level. For the complex formation channel, however, a different transition state has been located; the geometry and energetics of which are more consistent with experimental findings. Calculations of a few direct trajectories have been carried out to investigate the possible reason for the significant mode enhancement observed experimentally for the H-abstraction channel. Although none of them is reactive, a trajectory with an asymmetric C_2H bend excitation exhibits a clear signature for being more reactive than those without vibrational excitation or with a symmetric bend excitation.

K. Morokuma, Q. Cui, and Z. Liu, Potential Energy Surfaces and Their Dynamic Implications --- Non-adiabatic transition state theory for spin-forbidden reaction $CH(^2P)$ + N_2 and channel and mode selectivity in ion-molecule reactions: $C_2H_2^+$ + NH_3 and $C_2H_2^+$ + CH_4, Faraday Discussion, **110**, 71-89 (1998).

Accurate density functional and ab initio calculations have been performed to study the potential energy surfaces and their implications to kinetics and dynamics for the following reactions. I. Spin-forbidden reaction $CH(^2P)$ + N_2 → HCN + $N(^4S)$. Potential energy surface characteristics are calculated and used to evaluate the overall rate using the non-adiabatic transition state theory. II. Gas-phase ion-molecule reactions. A. $C_2H_2^+$ + NH_3. Potential energy surfaces have been calculated and the mechanism of efficient charge transfer and proton transfer competing with stable complex formation is discussed. B. $C_2H_2^+$ + CH_4. Mode-enhancement effect has been elucidated in terms of the new transition state and by direct trajectory calculations.

A-3. Mechanism of the $C_2H_2^+$ + methanol reaction.

S. Irle and K. Morokuma, Ab initio and density functional study on the mechanism of the $C_2H_2^+$ + methanol reaction, J. Chem. Phys., **111**, 3978-3988 (1999).

High level ab initio (G2MS and CASSCF) and density functional (B3LYP) calculations were carried out to study the mechanism of the ion-molecule reaction $C_2H_2^+$ + CH_3OH for four reaction channels: hydride abstraction from methanol (HA), proton transfer from acetylene cation (PT), charge transfer (CT) and covalent complex formation (CC) channel. For the CT channel, two pathways have been found: a usual non-adiabatic pathway via A'/A" seam of crossing and a low energy adiabatic pathway through an initial intermediate; the latter may be the dominant process with favorable energies and a large impact parameter. The HA process involves a low-energy direct intermediate and a very low barrier to form C_2H_3 + CH_2OH^+ and is also energetically favorable. The PT processes require passage over a high-energy transition state and are not important. One of the experimentally unobserved CC channels, formation of the COCC skeleton, is energetically favorable and there is no energetic reason for it not to take place; a "dynamic bottleneck" argument may have to be invoked to explain the experiment. The increase in reaction efficiency with the CC stretch excitation may be justified by considering the TSs for two CT pathways, where the CC distance changed substantially from that in the reactant $C_2H_2^+$. Very qualitatively, the $C_2H_2^+$ + CH_3OH potential energy surface looks more like that of the $C_2H_2^+$ + NH_3 system than the $C_2H_2^+$ + CH_4 system, because of the differences in the ionization potentials: NH_3 ~ CH_3OH < C_2H_2 < CH_4.

A-4. The mechanism of the ion-molecule reaction of O^+ (^4S) + C_2H_2.

K. Fukuzawa, T. Matsushita, K. Morokuma, D. J. Levandier, Y. Chiu, R. A. Dressler, E. Murad, A. Midey, S. Williams, and A. A. Viggiano, An ab initio and experimental study of vibrational effects in low energy O^+ + C_2H_2 charge-transfer collisions, J. Chem. Phys., **115**, 3184-3194 (2001).

Theoretical and experimental studies are performed to elucidate the low energy charge-transfer dynamics of the reaction, O^+ (^4S) + C_2H_2 (X $^1\Sigma_g^+$) → O + $C_2H_2^+$. In particular, the role of the low-frequency acetylene bending modes (612 and 730 cm^{-1}) in promoting charge transfer was examined. High temperature guided-ion beam measurements are carried out over the energy range from near-thermal to 3 eV at 310 and 610 K. The charge-transfer cross sections are found to decrease up to 0.5 eV, to have a constant value at intermediate energies between 0.5 and 1.5 eV, and then to dramatically increase above a threshold of a spin-allowed process determined to be at 1.7 eV. A bending vibrational enhancement of ~8 is observed at intermediate energies. Thermal energy rate coefficients are measured in a variable temperature-selected ion flow drift tube apparatus from 193 to 500 K. At each temperature, a negative energy dependence is observed. In order to elucidate the reaction mechanism in detail, high level ab initio calculations using Complete Active Space Self-Consistent Field (CASSCF) and Multi-Reference Single

and Double excitation Configuration Interaction (MRSDCI) methods have been performed. The results indicate that the charge transfer reaction occurs at an early stage via nonadiabatic transition between quartet and doublet states. There is a weak van der Waals minimum at the entrance channel between O^+ (^4S) and C_2H_2 with the relative energy of -1.51 kcal/mol. The minimum of the quartet/doublet crossing seam (Q/D MSX), where the spin-forbidden nonadiabatic transition is most likely to take place, lies very near this minimum at $R_{CO} = 4.06$Å, $R_{CC} = 1.20$Å, and $\angle CCH = 166.6°$ with a relative energy of -1.48 kcal/mol. After the nonadiabatic transition the system propagates on the doublet surface to reach the exothermic $O(^1D) + C_2H_2^+(\tilde{X}\,^2\Pi_u)$ products. No energy barrier exists on the reaction pathway, strongly suggesting that the reaction should occur at low energy with a negative energy dependence, which is consistent with the experiment. The Q/D MSX has a bent acetylene moiety, which suggests that the excitation in bending modes will enhance the reaction, in agreement with the experiment.

A-5. Potential energy profile and mechanism of ion-molecule reaction: $CH_4 + O_2^+$ ($^2\Pi_g$).

S. Irle and K. Morokuma, Ab initio investigation of the potential energy profiles of gas phase $CH_4 + O_2^+$ ($^2\Pi_g$) reaction system, J. Chem. Phys., **114**, 6119-6127 (2001).

High level ab initio and density functional calculations of the ground state potential energy profiles were carried out to study the mechanism of the ion-molecule reaction $CH_4 + O_2^+$ (X $^2\Pi_g$) for four reaction channels: insertion of O_2^+ into the C-H bond of methane (INS), hydride abstraction from methane (HA), charge transfer (CT), and O-O cleavage path (OO) after INS process to give CH_2OH^+ + OH. Common to these channels are initial encounter complexes, and our calculations match very closely experimental estimates for binding energies. The INS channel proceeds through CH_4OO^+ and gives a deep minimum corresponding to exothermic and metastable intermediate CH_3OOH^+. This species can easily eliminate H to give CH_2OOH^+, a product observed experimentally. For the slightly endothermic HA channel to give CH_3^+ + OOH, two pathways were found: a direct pathway (likely to dominate at higher collision energy) from the encounter complex via an HA transition state at 5.8 kcal/mol above the reactants, and an indirect pathway with a slightly smaller energy requirement consisting of elimination of OOH from the INS intermediate CH_3OOH^+. A transition state with a high energy requirement of 15 kcal/mol was found for O-O cleavage from CH_3OOH^+, consistent with the experimental finding that O-O cleavage occurs at high energies. It was also found that the seam of crossing between two potential surfaces is facilitated and therefore the CT channel is promoted by the O-O stretching and the methane deformation vibrations, again consistent with the experimental results.

B. Potential Energy Surfaces of Ions
B-1. Structure and spectroscopy of O_3^- ion.
Q. Cui and K. Morokuma, Ab initio studies on the electronic excited states and photodissociation of O_3

anion, J. Chem. Phys., **108**, 7684-7694 (1998).

Extensive ab initio calculations have been performed for the low lying electronic states of O_3^- to elucidate the mechanism of photodissociation processes. The identity of the mysterious state implied by the recent experiment of Continetti et al. has been discussed based on the current calculations. Calculations reveals that $^2B_2$ is a truly bound state favoring a strongly bent geometry with $\angle O$-O-O~90.0°, and crosses with the X $^2B_1$ at a similar angle. Therefore if O_3^- is produced in a highly bent geometry, $^2B_2$ might be preferentially populated. The large transition dipole moment and the vertical excitation energy for $^2B_2 \rightarrow ^2A_1$ also suggest that $^2B_2$ may be electronically excited efficiently to $^2A_1$ at the wave length of 523nm. The computed energetics of $^2B_2$ and $^2B_1$ and the corresponding dissociation limits may explain the larger maximum KER observed in the second experiment of Continetti and the smaller O_2-O^- bond energy derived from the experiment of Hiller, if we assume that $^2B_2$ is the parent state in both cases. Furthermore, meta-IRC calculations suggest rather different final state distribution of the photofragments from $^2B_1 \rightarrow ^2A_2$ and $^2B_2 \rightarrow ^2A_1$ processes, in qualitative agreement with the experimental observations. Although the vibrationally excited ground state O_3^- might also produce rotational hot, vibrational cold photofragments through the angular dependence of the seam between the two diabatic excited ^2A"states, the exact effect of parent vibrational excitation requires future dynamics calculations. At the current stage, our calculations strongly support that the $^2B_2$ electronic state has been accessed in the second experiment of Continetti et al.

B-2. Structure, spectroscopy and reaction of $(N_2O:H_2O)^+$ cation cluster.

J. E. Stevens, M. C. Holthausen, and K. Morokuma, The Potential Energy Surface of the $(N_2O \cdot H_2O)^+$ Cluster Cation, J. Chem. Phys., **111**, 7766-7773 (1999).

The ground state potential energy surface of the $(N_2O \cdot H_2O)^+$ cluster cation is explored with ab initio and density functional theories. B3LYP optimizations are used to determine the structure of the products of the dissociation of the cluster ions as well as possible structures for the clusters themselves and transition states that connect various minima. Energetics for all optimized structures are determined with the G2M(RCC,MP2) method. The results are used to interpret collision-induced dissociation (CID) experiments which study the cluster ion, and which find that the cluster dissociates to form $H_2O^+ + N_2O$, $N_2OH^+ + OH$, and $N_2O^+ + H_2O$ products. The calculations an $(N_2O$--$OH_2)^+$ complex as well as a similar $(H_2O$-$N_2O)^+$ complex, and show that these complexes access the experimentally observed $H_2O^+ + N_2O$ products and $N_2OH^+ + OH$ products without any intervening reverse barrier. The stability of both these complexes, approximately -20 kcal/mol relative to the $H_2O^+ + N_2O$ products, agrees well with experimentally determined CID thresholds for all products. Additional calculations of the ground state potential energy surface of the cluster investigate the possibility of the formation of other products. Some preliminary studies of the excited states of the cluster cation are also performed; the results of these

calculations lend insight into experimental photodissociation studies of the cluster ions. Mechanisms for the formation of $H_2O^+ + N_2O$, $N_2OH^+ + OH$, and $N_2O^+ + H_2O$ products following photoexcitation of the cluster ions are discussed; the $H_2O^+ + N_2O$ and $N_2OH^+ + OH$ products must be formed from a surface-hopping from an excited electronic state to states which correlate to ground state products. Similarly, $N_2O^+ + H_2O$ products may be formed from collision induced dissociation of clusters only by means of a surface-hopping mechanism.

B-3. Electronic structure of triply charged molecular ions N_2^{+3}.

D. Bandrauk, D. G. Musaev and K. Morokuma, Electronic States of the Triply Charged Molecular Ion N_2^{3+} and Laser Induced Coulomb Explosion, Phys. Rev. A, **59**, 4309-4315 (1999).

Potential-energy curves for the low-lying doublet and quartet states of various symmetries (Π_g, Π_u, Σ_g, and Σ_u) of the triply charged N_2^{3+} mol. cation are studied using quantum ab initio methods. These states correlate asymptotically to the $N_2^+ + N^+$ at. fragments. No stable (bound) states are found to occur in the midst of many Coulomb repulsive potentials. The potentials are shown to follow a pure Coulomb repulsion law at R≥5 bohr. The most relevant configurations are enumerated for discussion of recent laser Coulomb explosion and imaging experiments.

B-4. Structure and spectroscopy of Cl_3^- ion.

A. L. Kaledin, M. C. Heaven, K. Morokuma and D. M. Neumark, Cl_3^- electron photodetachment spectrum: measurement and assignment, Chem. Phys. Lett., **306**, 48-52 (1999).

An electron photodetachment spectrum of Cl_3^- is reported for 193 nm (6.42eV) excitation. The spectrum was assigned using high-level ab initio calculation for the Cl_3 radical and the Cl_3^- ion. A broad band centered around 1.25 eV (electron kinetic energy) has been assigned to the Cl_3^- (X $^1\Sigma_g^+$) → Cl_3 (X $^2\Pi_u$) and Cl_3 (1 $^2\Sigma_g^+$) transitions. Vertical photodetachment accesses the transition state region for the Cl exchange reaction: $Cl + Cl_2$ → $Cl_2 + Cl$. A narrow doublet band at 0.55 eV is assigned to the Cl_3^- (X $^1\Sigma_g^+$) → Cl_3 (1 $^2\Pi_g$) transition, split by spin-orbit interaction.

B-5. The photoelectron spectroscopy of the IHBr and IDBr anions.

A. Kaledin, S. Skokov, J. M. Bowman and K. Morokuma Theoretical study of the photoelectron spectroscopy of the IHBr and IDBr anions, J. Chem. Phys., **113**, 9479-9487 (2000).

The coupled cluster method with a large basis set with quasi-relativistic effective core potentials on the halogens was utilized to investigate the ground electronic state, $X^1\Sigma^+$, of the IHBr anion. A semi-

global, three-dimensional potential energy surface was obtained via spline interpolation of ab initio data. Variational rovibrational calculations were carried out with this potential energy surface, and assignment of fundamentals and low lying overtones as well as combination bands is presented for IH(D)Br anions. Photodetachment spectra for IH(D)Br$^-$ + hν $\rightarrow$ [IH(D)Br] + e$^-$ were computed using three-dimensional time independent real and complex L^2 methods and a recently developed real L^2 wave packet propagation technique; all methods employed a previous London-Eyring-Polanyi-Sato empirical potential for the neutral system. Well resolved fine structure is found in photodetachment spectra of IHBr$^-$. This structure is assigned to bending excitation based on analysis of the wavefunctions and the neutral potential energy surface near the Franck-Condon region. This fine structure is largely eliminated in the IDBr$^-$ spectrum. The photodetachment spectrum for the first excited asymmetric stretch of IHBr$^-$ shows a new feature that is associated with sampling of the transition state region of the neutral surface. Spin-orbit corrected multi-reference configuration interaction calculations indicate that the first excited electronic state is only about 0.06 eV above the ground electronic state of the neutral IHBr system in the Franck-Condon region. The model empirical potential used in the calculations of photodetachment spectra is shown to have roughly the average behavior of these two ab initio potentials.

C. Potential Energy Surfaces for Photochemical Reactions and Nonadiabatic Processes.
C-1. Mechanism of photodissociation of isocyanic acid, HNCO.

J. E. Stevens, Q. Cui, and K. Morokuma, An ab initio Study of the Dissociation of HNCO in the S$_1$ Electronic State, J. Chem. Phys., **108**, 1452-1458 (1998).

Regions of the S$_1$ potential energy surface of HNCO relevant to N-H and C-N bond photodissociation have been investigated with ab initio calculations. Geometries of minima and transition states on S$_1$ as well as those of the product photofragments and the HNCO ground state have been optimized with the CASSCF method, and their energies calculated with MRSDCI and CASPT2 methods. Deep planar trans and cis minima exist on the S$_1$ surface, and are connected by transition states for isomerization. The S$_0$$\rightarrow$S$_1$ electronic transition is brighter for trans configurations than for cis, and the initial excitation and dynamics is most likely to proceed through trans configurations. The N-H fission on S$_1$ has a substantial barrier; it occurs more easily through the planar cis transition state which is about 20 kcal/mol above the dissociation threshold than through the trans transition state. The C-N fission on S$_1$ can take place both via the planar trans and the planar cis transition state with a low barrier over the dissociation threshold; the reverse barrier is estimated to be a few kcal/mol.

A. L. Kaledin, Q. Cui, M. C. Heaven and K. Morokuma, Ab initio Theoretical Studies on Photodissociation of HNCO upon S$_1$(^{1}A") $\leftarrow$ S$_0$(^{1}A') Excitation: The Role of Internal Conversion and Intersystem Crossing, J. Chem. Phys., **111**, 5004-5016 (1999).

Photodissociation of isocyanic acid, HNCO, was studied with high-level ab initio methods. Geometry optimizations of stationary points and surface crossing seams were performed with the complete active space self-consistent field (CASSCF) method, and the energetics were re-evaluated with single-point second-order multireference perturbation theory (CASPT2). The three product channels that participate in the photodissociation process are: [1] $HN(X^3\Sigma^-)$ + CO at 86.0 (calculated 79.6) kcal/mol, [2] H + $NCO(X^2\Pi)$ at 109.7 (108.7) kcal/mol, and [3] $HN(a^1\Delta)$ + CO at 122.2 (120.8) kcal/mol. The four electronic states, S_0, S_1, T_1 and T_2, that interconnect these channels were studied in detail. S_1 exhibits dissociation barriers to both, channel [2] and [3], whose respective reverse heights are 11.3 and 1.2 kcal/mol, in good agreement with experiment as well as previous theoretical works. The two triplets, T_1 and T_2, show barriers of similar heights for HN bond fission, while S_0 has no barriers to either channel. Various key isomerization transition states as well numerous minima on the seam of surface crossings (MSX's) were also found. At photoexcitation energies near channel [3] threshold, products to channel [3] are likely to be formed via: $S_1 \rightarrow$[3] (if enough energy in excitation) and $S_1 \rightarrow S_0 \rightarrow$[3]. Channel [2] can be formed via: $S_1 \rightarrow S_0 \rightarrow$[2]; (HN-mode quanta)+$S_1 \rightarrow T_1 \rightarrow$[2]; $S_1 \rightarrow T_2 \rightarrow$[2]; $S_1 \rightarrow T_2 \rightarrow T_1 \rightarrow$[2], and channel [1] via $S_1 \rightarrow S_0 \rightarrow T_1 \rightarrow$[1], $S_1 \rightarrow T_1 \rightarrow$[1] and $S_1 \rightarrow T_2 \rightarrow T_1 \rightarrow$[1]. At higher photoexcitation energies $S_1 \rightarrow$ [3] is expected to be dominant while channel [2] with higher activation energy is expected to drop rapidly. Also addressed are such important issues as the impact of vibrationally excited HN mode on channel [2] yield, and the band origin of the $S_1 \leftarrow S_0$ excitation spectrum.

C-2. Mechanism of spin-forbidden reaction $CH(^2P)$ + N_2 → HCN + $N(^4S)$

Q. Cui and K. Morokuma, The spin-forbidden reaction $CH(^2P)$ + N_2 → HCN + $N(^4S)$ revisited. I. — Ab initio study on the potential energy surfaces, Theo. Chem. Acc., **102**, 127-133 (1999).

High level ab initio electronic structure theories have been applied to investigate the detailed reaction mechanism of the spin-forbidden reaction of $CH(^2\Pi)$ + N_2 → HCN + $N(^4S)$. The G2M(RCC) calculations provide accurate energetics for the intermediates and transition states involved in the reaction, whereas the B3LYP/6-311G(d,p) method overestimates the stability of some intermediates as much as ~10kcal/mol. A few new structures have been found on both the doublet and quartet electronic states, which are mainly involved in the dative pathways. However, due to the higher energies of these structures, the dominant mechanism remains to be the one involving the C_{2v} intersystem crossing step. The C_{2v} MSX structures and the spin-orbit coupling between the doublet and quartet electronic states are rather close to those found in previous studies. Vibrational frequencies orthogonal to the norm of the

seam have been calculated at the MSX from the first principle, which have been applied in a separate publication to calculate the rate of the titled reaction with a newly proposed non-adiabatic transition state theory for spin-forbidden reactions.

Q. Cui, K. Morokuma, J. M. Bowman and S. J. Klippenstein, The spin-forbidden reaction $CH(^2P) + N_2$ $\rightarrow$ HCN + $N(^4S)$ revisited. II. — Non-adiabatic transition state theory and application. J. Chem. Phys., **110**, 9469-9482 (1999).

Transition state theory is extended straightforwardly to treat non-adiabatic processes and applied to study the rate constant of the spin-forbidden reaction $CH(^2\Pi) + N_2 \rightarrow HCN + N(^4S)$. A one-dimensional model was set up to calculate the intersystem crossing probability with the distorted wave approximation and using an ab initio value of the spin-orbit coupling. The effect of orthogonal degrees of freedom was then considered by energy convolution with the vibrational frequencies, obtained from ab initio calculations, orthogonal to the crossing seam at the minimum of the seam of crossing (MSX), also obtained from ab initio calculations. An expression for the cumulative reaction probability, N(E), of the reaction was obtained by a straightforward extension of the unified statistical theory, where the MSX was treated as a transition state. The calculated thermal rate constant, k(T), seems to be too low by two orders of magnitude compared to experimental measurements and an empirical transition state study where empirical vibrational frequencies at the MSX are lower by a factor of two than those derived here. The disagreement strongly suggests that the current treatment of the multi-dimensional dynamics needs to be improved. In particular, it may be a poor assumption that spin-forbidden transition takes place with uniform probability on the seam in the case we are considering.

C-3. Ab initio direct-trajectory study of the photodissociation of ClOOCl.

L. Kaledin, and K.Morokuma, An ab initio direct-trajectory study of the photodissociation of ClOOCl, J. Chem. Phys., **113**, 5750-5762 (2000).

The photodissociation of chlorine peroxide, ClOOCl, is studied with classical trajectories where the energy and gradient are computed on the fly by means of the state-averaged (sa) CASSCF with the DZP(+) basis set. We show that six electronically excited states are involved in the process of decomposition, which proceeds via several competing pathways and at least three electronically unique fragment channels. The problem is treated in 4D (C_2 constraint) and 5D (planar constraint) frameworks in order to model the mechanisms of synchronous and asynchronous or stepwise dissociation, respectively. A single trajectory with the initial conditions of a non-vibrating non-rotating molecule is propagated on each excited state surface for an average time of 10 fs for the purposes of determining the early stages of bond breaking. We show that even in such a short propagation time the pathway competition can be more or less unambiguously understood. The results indicate that in the regime of a 308 nm photolysis, the major dissociation fragments are Cl atoms and O_2 molecules, both in the ground state. The higher energy

regime of a 248 nm photoexcitation yields additional fragments, e.g., $ClO(X^2\Pi)$, $O(^3P)$ and $ClOO(X^2A"$, $1^2A')$. We have achieved an overall qualitative agreement with experiment that more than 70% of the available energy is transferred into the translational energy of the products for the case of the synchronous concerted dissociation. In all the cases, the rotational excitation of produced molecular oxygen is very high, while its vibration is in v=0. Implications of the results on the stratospheric ozone depletion cycle are also presented.

C-4. An initio direct-trajectory study of the photodissociation of ketene.

A. L. Kaledin, J. Seong and K. Morokuma, Predominance of Non-equilibrium Dynamics in the Photodissociation of Ketene in the Triplet State, J. Phys. Chem. A, **105**, 2731-2737 (2001).

The photodissociation of ketene is studied using direct surface hopping classical trajectories where the energy and gradient are computed on the fly by means of state-averaged complete active space self-consistent field with a double zeta polarized basis set. Three low-lying electronic states, singlets S_0, S_1 and triplet T_1, are involved in the process of photodissociation of triplet state ketene. We propagated a trajectory, starting at the Franck-Condon geometry on S_1, and branched it out into many child trajectories every time the propagating potential energy surface (PES) crossed with another PES. The major photodissociation pathway to the triplet products was found to be $S_1 \rightarrow S_0 \rightarrow T_1 \rightarrow CH_2(X\,^3B_1) + CO(X$

$^1\Sigma^+)$. It has been found that 1) the S_0-T_1 non-adiabatic transition creates the T_1 species non-statistically at restricted regions of phase space, and 2) a large fraction of the T_1 species thus created dissociates almost immediately, leaving no time for equilibration of internal degrees of freedom. Whether a specific T_1 trajectory dissociates fast or not is determined by the amount of C-C stretch vibration at the S_0-T_1 branch point. In essence, the above observations suggest strongly that the T_1 photodissociation process is highly non-statistical, thus making equilibrium-based statistical theories inapplicable for computing the dissociation rate.

C-5. The symmetry breaking and its effect on the potential surface of NO_3.

W. Eisfeld and K. Morokuma, A detailed study on the symmetry breaking and its effect on the potential surface of NO_3, J. Chem. Phys., **113**, 5587-5597 (2000).

The tenacious symmetry breaking of the electronic wave function of the nitrate radical (NO_3) and its effect on the ground-state potential energy surface is investigated in detail. The symmetry breaking of Hartree–Fock wave functions results from a dominance of the orbital localization effect over the resonance effect and leads to three different solutions, one symmetrical and two distorted ones, for the same electronic state. The respective equilibrium geometries of these solutions are points on different potential surfaces, making their comparison meaningless. The resonance effect is promoted by dynamic as well as static electron correlation. However, the dynamic correlation methods [e.g., many-body

perturbation theory (MBPT) and coupled-cluster single double (CCSD)] cannot overcome the symmetry breaking of the reference function and the problem of multiple solutions persists. The symmetry breaking can be avoided by the complete active space self-consistent field (CASSCF) approach that yields unique, single-valued surfaces for all electronic states. However, a sufficiently large and appropriately selected active space has to be used to avoid unphysical distortion of the wave function. Still the orbital localization effect leads to equilibrium geometries of C_{2v} symmetry which strongly depend on the state-averaging of the CASSCF wave function. Multireference single double configuration interaction (MR-SDCI) wave functions are also free of symmetry breaking, if the reference orbitals are and if the configuration space is invariant under the symmetry operations. MRCI geometry optimizations only result in D3h symmetric structures with bond lengths and harmonic frequencies in close agreement with experimental data.

W. Eisfeld and K. Morokuma, Ab initio investigation of the vertical and adiabatic excitation spectra of NO_3, J. Chem. Phys., **114**, 9430-9440 (2001).

The ground and excited electronic states up to approximately 100 000 cm^{-1} of the nitrate free radical (NO_3) are investigated by complete active space self-consistent-field (CASSCF) and mulitreference–singles doubles configuration interaction calculations. Extended basis sets, containing polarization and diffuse functions, and an active space consisting of 13 orbitals and 17 electrons are used. A total of 28 electronic states is obtained within the D_{3h} framework which split into 44 states in C_{2v}. All calculated states are valence states and their character is discussed in detail. Oscillator strength and radiative lifetimes are determined from the CASSCF wave functions and give evidence for a strong transition that was not yet known experimentally. For the experimentally observed ^2E and ^2E states equilibrium geometries, harmonic frequencies, and adiabatic excitation energies are calculated in excellent agreement with experimental data. Important new insight is gained about the role of the low-lying electronic states in the photodissociation and the mechanism of this process is discussed.

C-6. Spin-allowed and Spin-forbidden Pathways of the Gas Phase Reactions of $O(^3P)$ + C_2H_5I,

J. E. Stevens, Q.Cui and K. Morokuma, An ab initio Investigation of Spin-allowed and Spin-forbidden Pathways of the Gas Phase Reactions of $O(^3P)$ + C_2H_5I, J. Chem. Phys., **108**, 1544-1551 (1998).

The singlet and triplet potential energy surfaces involved in the gas phase reactive collisions of $O(^3P)$ and C_2H_5I have been studied with ab initio electronic structure computations. The collisions produce both spin-forbidden HOI + C_2H_4 and spin-allowed OI + C_2H_5 products. The calculations indicate that HOI is formed via a triplet complex and through a triplet/singlet intersystem crossing, followed by passage through a singlet intermediate and transition state for the intramolecular abstraction of β-hydrogen. All the relevant structures for this pathway are lower in energy than the reactants, and this

pathway is accessible even at low impact energies. The calculations also indicate that OI may be formed by two channels. One is the same to the above singlet pathway up to the singlet intermediate, which now dissociates endothermically without barrier to give the products. The second channel is the direct dissociation of the triplet intermediate, and is open only when an enough excess energy to surmount a triplet transition state is provided. The product energy distribution is also discussed based on the structures of transition states.

D. Potential Energy Surfaces of Open-Shell Molecules.

D-1. Electronic structure of C_2H.

Q. Cui and K. Morokuma, Ab initio Studies on the Electronic Excited States of C_2H, J. Chem. Phys., **108**, 626-636 (1998).

High level ab initio calculations have been carried out to study seven electronic states of C_2H. The calculated equilibrium structure, energetics and vibrational frequencies for the 3 $^2A'$ state at the CASPT2/PVTZ level are in good agreement with those obtained experimentally by Hsu et al. The transition dipole moments from the ground state C_2H to electronic excited states depend sensitively on the H-C-C bending angle and often peak at non-linear configurations. Based on this and the dissociation behavior of the excited states, we predict A $^1\Pi_u$ and c $^3\Sigma^+_u$ C_2 fragments to be rich in population, the former of which is experimentally detected recently by Jackson et al. The ground X $^1\Sigma^+_g$ and the a $^3\Pi_u$ state C_2 are expected to be formed via the non-adiabatic process 3 $^2A' \rightarrow$ 2 $^2A'$ or 4 $^2A' \rightarrow$ 3 $^2A' \rightarrow$ 2 $^2A'$, which is in accord with the experimentally observed lifetime pattern by Hsu et al. No reverse barrier for CC-H dissociation was found on the X and A electronic states of C_2H in the linear configuration. The 2 $^2A'$ state, however, develops a distinct "barrier" (not a true saddle point) along dissociation coordinate when the H-C-C is significantly bent, due to the interaction with upper electronic state. Since the 2 $^2A'$ state energetically prefers a linear dissociation, we suspect that the upper bound of the CC-H bond energy measured by Hsu et al. is not severally affected by this "barrier".

D-2. Structure, electronic structure and spectroscopy of Cl_3.

A. L. Kaledin, M. C. Heaven, W. G. Lawrence, Q. Cui, J. E. Stevens and K. Morokuma, Ab initio Molecuclar Orbital Study of the Trichlorine Radical, Cl_3, J. Chem. Phys., **108**, 2771-2783 (1998).

We report a rigorous ab initio study of the ground and low-lying excited-state potential energy surfaces (PESs) of the Cl_3 radical at CASSCF, CASPT2 and MRSDCI levels of theory. The ground state has two $Cl..Cl_2$ van der Waals complexes, $\tilde{X}L$ and $\tilde{X}'B$. The linear asymmetric minimum ($\tilde{X}L$) is $^2\Pi$, with a Cl-Cl distance r = 3.90 bohr, and a Cl-M (M: the Cl_2 center-of-mass) distance R = 8.70 bohr. The bent asymmetric minimum ($\tilde{X}'B$) is of $^2A'$ symmetry, with r = 3.90 bohr, R = 6.85 bohr, and the angle between $\hat{r}$ and $\hat{R}$, $\gamma = 68.4°$. Spin-orbit CI predicts that the global minimum is linear $\tilde{X}L$ ($^2\Pi_{3/2}$) with a

bond dissociation energy of $D_e(Cl_2(X)-Cl)$ of 280 cm^{-1}. Low-lying doublet excited states have only one strongly bound structure, a linear symmetric $\tilde{A}L$ (1 $^2\Pi_g$) state with a bond distance of 4.67 bohr. This state is bound by approximately 4,300 cm^{-1} with respect to the $Cl_2(^3\Pi_u)$ + Cl asymptote, and its minimum lies about 8,700 cm^{-1} above the $\tilde{X}L$ van der Waals minimum. Transition dipole moment calculations show that the $\tilde{A} - \tilde{X}$ transition is fully allowed. Two bound quartet minima were located. The most deeply bound was **QD3h** ($1^4A_1'$) with a D_{3h} equilibrium geometry (r = 5.00 bohr) about 11,300 cm^{-1} above $\tilde{X}L$. The other state, **QC2v** (1^4A_2) had a C_{2v} equilibrium geometry (r_1 = 4.83 bohr and θ = 101.7°) and an energy of about 13,500 cm^{-1} relative to $\tilde{X}L$. Although $Cl_3(\tilde{X})$ is shown to be unstable, the present results support the notion that Cl_3 participates in Cl atom recombination processes. However, the energies and transition moments of the low-lying excited states are not consistent with electronic spectra that have been tentatively assigned to Cl_3

E. Dynamics and Kinetics in the Ground Electronic State.
E-1. H and H_2 elimination pathways from methane, ethane and propane.
S. Irle and K. Morokuma, A molecular orbital study on H and H_2 elimination pathways from methane, ethane and propane, J. Chem. Phys., **113**, 6139-6148 (2000).

Decomposition pathways for propane, as well as methane and ethane for comparison, in its ground electronic state were studied using density functional and high accuracy ab initio calculations. The reaction pathways were characterized by locating the transition states and following the intrinsic reaction coordinate. Atomic hydrogen as well as molecular hydrogen elimination pathways were investigated, including three deuterated propane species for comparison with experiment. The methyl and ethyl groups in propane are found to stabilize trransition states and radical/biradical intermediates along the reaction pathways. For propane, 2,2-elimination of an hydrogen molecule is found to be the dominat molecular elimination pathway, in agreement with recent photochemical experiments. We find 1,1-elimination to be the next important molecular elimination pathway, followed by 1,2-elimination, which disagrees with the experimental result favoring 1,2- over 1,1-elimination.

E-2. Dipole moments of highly vibrationally excited HCN.
J. M. Bowman, S. Irle, K. Morokuma, and A. Wodtke, Dipole moments of highly vibrationally excited HCN: theoretical prediction of an experimental diagnostic for delocalized states. J. Chem. Phys., **114**, 7923-7934 (2001).

Vibrational state specific dipole moments are diagnostic of the degree of localization of vibrational states in highly vibrationally excited HCN. Using a newly calculated global ab initio dipole moment function and previously calculated highly accurate vibrational wave functions, we show that delocalized (i.e. isomerizing) vibrational states of HCN possess markedly lower dipole moments than localized HCN

or HNC states. We also show that the vibrational quantum number dependence of the dipole moment can be used to distinguish delocalized states from localized Franck-Condon-dark states that are made observable by perturbations with localized Franck-Condon-bright states. Furthermore, using classical trajectory analysis we introduce and describe a new experimental approach to obtain these data, which relies on combining optical pumping and state specific molecular transport with hexapoles. With this method it is possible to determine state specific dipole moments with high accuracy and precision.
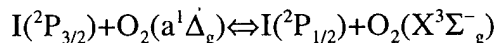
F. Potential Energy Surfaces for the Dynamics of Chemical Laser Systems.

In collaboration with Prof. Mike Heaven and the Chemical Laser group at the Air Force Research Laboratory, Kirtland Air Force Base, we have undertaken computational studies on the potential energy surfaces and dynamics of chemical reactions and energy transfer processes which control the efficiencies of chemical laser systems. In particular, we have worked on the $I + O_2$ and the $I + NCl$ systems.

F-1. A surface-hopping trajectory study for theoretical prediction of the rate constant for the $I(^2P_{3/2}) + O_2(a^1\Delta_g) \Leftrightarrow I(^2P_{1/2}) + O_2(X^3\Sigma^-_g)$ energy transfer process.

A. L. Kaledin, M. C. Heaven, and K. Morokuma, Ab initio Potential Energy Surfaces for the $I(^2P_{3/2}) + O_2(a^1\Delta_g) \Leftrightarrow I(^2P_{1/2}) + O_2(X^3\Sigma^-_g)$ Energy Transfer Process, Chem. Phys. Lett., **289**, 110-117 (1998).

Ab initio electronic structure calculations have been used to investigate the electronic energy transfer process

$$I(^2P_{3/2})+O_2(a^1\Delta_g) \Leftrightarrow I(^2P_{1/2})+O_2(X^3\Sigma^-_g)$$

Potential energy surfaces for all states associated with the reactants and products were obtained using CASSCF and CASPT2 methods, including the effective one-electron spin-orbit Hamiltonian. Surfaces correlating with the above reactants and products were all found to be non-bonding. Shallow van der Waals minima were predicted at long range. Surface crossings were found at energies below the $I(^2P_{3/2})+O_2(a^1\Delta_g)$ asymptote. It is probable that these crossings are responsible for the efficient transfer of electronic energy in this system.

L. Kaledin, M. C. Heaven, K. Morokuma, Theoretical prediction of the rate constant for $I + O_2(a^1\Delta_g)$ electronic energy transfer: a surface-hopping trajectory study, J. Chem. Phys., **114**, 215-224 (2001).

The temperature dependence of the rate constant for the electronic energy transfer process $I(^2P_{3/2}) + O_2(a^1\Delta_g) \rightarrow I(^2P_{1/2}) + O_2(X^3\Sigma^-_g)$ has been studied theoretically. Seven ab initio diabatic potential energy surfaces, four for the entrance channel and three for the exit channel, and the coupling elements between them were adopted. Energy transfer dynamics was simulated with the semi-classical surface-hopping trajectory calculation, using Tully's "fewest switches" model for electronic transition. Approximately

5×10^5 trajectories were statistically averaged over a range of impact parameters and collision energies to calculate thermal rate constants for the temperature range 10-300 K. It was found that collisions resulting in energy transfer were dominated by single hop trajectories. The calculated energy transfer rate constant was found to decrease smoothly with increasing temperature over the range 100-300 K. The predicted value was in excellent agreement with the experimental result for 150 K, but the calculations underestimate room temperature data by a factor of 1.6. The rate constant increases with decreasing energy because (i) long-range attractive forces draw slow moving collision partners together and, (ii) longer lifetime of slow collisions increases the probability of surface-hopping. It is also found that there is a competition between rotational relaxation of O_2(a) and electronic energy transfer

3. Publications.

The following 30 papers, supported in par by the present grant, have been published during the grant period.

Q. Cui and K. Morokuma, Ab initio Studies on the Electronic Excited States of C_2H, J. Chem. Phys., **108**, 626-636 (1998).

J. E. Stevens, Q. Cui, and K. Morokuma, An ab initio Study of the Dissociation of HNCO in the S_1 Electronic State, J. Chem. Phys., **108**, 1452-1458 (1998).

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Q. Cui, D. G. Musaev and K. Morokuma, Molecular orbital study of H_2 and CH_4 activation on small metal clusters. I. Pt, Pd, Pt_2 and Pd_2, J. Chem. Phys., **108**, 8418-8428 (1998).

A. L. Kaledin, M. C. Heaven, and K. Morokuma, Ab initio Potential Energy Surfaces for the $I(^2P_{3/2})$ + $O_2(a^1\Delta_g)$ $\Leftrightarrow$ $I(^2P_{1/2})$ + $O_2(X^3\Sigma^-_g)$ Energy Transfer Process, Chem. Phys. Lett., **289**, 110-117 (1998).

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A. D. Bandrauk, D. G. Musaev and K. Morokuma, Electronic States of the Triply Charges Molecular Ion N_2^{3+} and Laser Induced Coulomb Explosion, Phys. Rev. A, **59**, 4309-4315 (1999).

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4. Interactions/Transactions.

Consultative and advisory functions to other laboratories and agencies, especially Air Force and other DoD laboratories.

1. We have been in close contact with Dr. Viggiano of the Air Force Research Laboratory at the Hanscom Air Force Base concerning the interpretation of their ion-molecule experimental results.

2. We have been in close contact with Drs. Dressler and Ed. Murad of the Air Force Research Laboratory at the Hanscom Air Force Base, concerning the interpretation of the experimental results for their ion-molecule and other reaction system.

3. We, jointly with Professor Michael Heaven of our Department, are collaborating with the chemical laser group the Air Force Research Laboratory at the Kirkland Air Force Base, on the potential energy surfaces and dynamics relevant to COIL and NAIL chemical laser systems.

5. New inventions and patent disclosures.

None.

6. Honors/Awards.

Elected as the President of the International Academy of Quantum Molecular Science. From July 2000 – June 2003.